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Giorgio [DE/DE]; Schimmelpfennigstrasse 65, 40597
Düsseldorf (DE). GIORDANI, Paolo [IT/IT]; Via Cap-
puccini, 80/A, I-26013 Crema (IT). DEMERTZIS,
Ioannis [GR/IT]; Via Cadibona, 18, I-20122 Milano (IT).

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(71) Applicant (*for all designated States except US*): **HENKEL
KOMMANDITGESELLSCHAFT AUF AKTIEN**
[DE/DE]; Henkelstrasse 67, 40589 Düsseldorf (DE).

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(72) Inventors; and

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ning of each regular issue of the PCT Gazette.*

(75) Inventors/Applicants (*for US only*): **CORTELLARO**,



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(54) Title: AN ECONOMIC METHOD FOR RESTORING THE OXIDATION POTENTIAL OF A PICKLING SOLUTION

(57) Abstract: A process for pickling and/or passivating stainless steel, wherein the stainless steel is brought into contact with an aqueous treatment solution with a pH value of 2.5 or below, which contains Fe(III) ions which are reduced to Fe(II) ions during pickling, wherein Fe(II) ions are re-oxidized continuously or discontinuously by the injection or oxygen gas or of a gas mixture containing more than 10 % by volume of oxygen gas, and wherein a non-gaseous oxidizing agent is additionally added to said aqueous treatment solution as long as either the actual Fe(III) concentration is by more than 3 g/l lower than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is by more than 0.15 lower than the optimum Fe(III)/Fe(II) weight ratio, and the addition of the non-gaseous oxidizing agent is terminated when either the actual Fe(III) concentration is equal to or higher than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is equal to or higher than the optimum Fe(III)/Fe(II) weight ratio.

An economic method for restoring the oxidation potential of a pickling solution

This invention relates to a process for pickling and/or passivating special steel (also termed "stainless steel"). In general, technical steels are termed non-rusting or stainless if rust formation is prevented under normal environmental conditions, for example in the presence of atmospheric oxygen and moisture and in aqueous solutions. Most high-alloy, so-called corrosion-resistant or acid-resistant steels withstand relatively severe corrosion conditions, for example acids and salt solutions. These steels are generically referred to as special steels. A list of the technically most important special steels, together with the material numbers, identifications and alloy components, as well as the mechanical and chemical properties thereof are given in Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Vol. 22, pp. 106-112 and in German Industrial Standard DIN 17440, July 1985. Special steels are iron based alloys containing at least 10% chromium. The formation of chromium oxide on the material surface imparts to the special steels the corrosion-resistant character thereof.

Special steels may be sub-divided into the following families: austenitic steels, ferritic steels, martensitic steels, precipitation hardened steels and duplex steels. These groups differ in the physical and mechanical properties thereof, as well as in corrosion resistance, as a result of the various alloying constituents. Austenitic special steels are listed as special steels of the 200 and 300 Series. They are the most widely employed special steels and represent 65 to 85% of the special steel market. They are chemically characterized by a chromium content of > 17% and a nickel content of > 8%. They have a cubic face-centered structure and are outstandingly ductile and weldable. The most widely used of these steels is probably Type UNS S 30400 (Type 304), or "18/8". Modifications include S 32100 (stabilized with titanium) and S 34700 (stabilized with niobium). Alloys having higher contents of chromium, nickel or molybdenum are available and provide increased corrosion resistance. Examples are S 31600, S 31700, S 30900 and S 31000. The 200 Series of austenitic special steels has, on the other hand, a reduced nickel content and contains manganese instead.

When special steel is annealed, hot rolled, etc., a layer of scale forms on the surface, which destroys the desired shiny metallic appearance of the steel surface. This surface layer must therefore be removed after this production step. This removal may be effected by the pickling process according to the present invention. The oxide-containing surface

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layer to be removed differs fundamentally from the oxide layer on low-alloy steels or on carbon steels. Apart from iron oxides, the surface layer contains oxides of the alloying elements, for example chromium, nickel, aluminum, titanium or niobium. Particularly in hot rolling, there is an accumulation of chromium oxide in the surface layer. The oxide layer is accordingly enriched with chromium rather than iron. Conversely, this means that the steel layer immediately underneath the oxide layer is depleted in chromium. A pickling process using suitable acidic pickling solutions preferentially dissolves this chromium-depleted layer underneath the oxide layer, with the result that the oxide layer is removed.

After the pickling, the surface is chemically activated, which means that, in air, the surface once again becomes coated with an optically interfering surface layer. This may be prevented by passivating the freshly pickled surfaces after or during the pickling. This may be performed in treatment solutions similar to the pickling solutions, a higher redox potential being used for the passivation than for the pickling process. This special passivation step forms an optically invisible passivation layer on the metal surface, and the steel surface thereby preserves its shiny metallic appearance. Whether a treatment solution behaves in a pickling or passivating manner with respect to special steel depends, in the solutions according to the present invention, mainly on the established redox potential. Acidic solutions having pH values below about 2.5 have a pickling action if, on account of the presence of oxidizing agents, they have a redox potential in the range from about 200 to about 350 mV with respect to a silver/silver chloride electrode. If the redox potential is raised to values above about 350 mV, the treatment solution has a passivating effect.

Pickling processes for special steel are well-known in the art. Earlier processes use nitric acid-containing pickling baths. These often additionally contain hydrofluoric acid, which on account of its complexing action with respect to iron ions promotes the pickling process. Although such pickling baths are economically efficient and technically satisfactory, they have the serious ecological disadvantage that they emit considerable amounts of nitrogen oxides and release large amounts of nitrates into the waste water.

Intensive efforts have therefore been made in the art to find alternative pickling and passivating processes that do not use nitric acid. Fe(III) ions are a possible substitute for the oxidizing action of nitric acid. The concentration of Fe(III) ions is maintained by hydrogen peroxide, which is added continuously or batch wise to the treatment baths. Such pickling or passivating baths contain about 15 to about 65 g/l of trivalent iron ions.

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During the pickling process, trivalent iron ions are converted to the divalent form. At the same time, further divalent iron ions are dissolved out from the pickled surface. The pickling bath is thereby depleted in trivalent iron ions during the operation, while divalent iron ions accumulate. The redox potential of the treatment solution is thereby displaced, with the result that the solution finally loses its pickling action.

Divalent iron ions are oxidized back to the trivalent state by the continuous or batch wise addition of oxidizing agents, for example hydrogen peroxide, or other oxidizing agents, such as perborates, peracids or also organic peroxides. In this way, the redox potential necessary for the pickling or passivating action is maintained.

EP-B-505 606 describes a nitric acid-free process for the pickling and passivation of stainless steel, in which the material to be treated is immersed in a bath at a temperature of between 30 and 70 °C and which contains, at least at the beginning of the pickling process, at least 150 g/l of sulfuric acid, at least 15 g/l of Fe(III) ions, and at least 40 g/l HF. This bath furthermore contains up to about 1 g/l of additives, such as non-ionic surfactants and pickling inhibitors. Hydrogen peroxide is added continuously or batch wise to the bath in such amounts that the redox potential remains in the desired range. The other bath constituents are also replenished so that the concentration thereof remains within the optimum operating range. The pickling bath is agitated by blowing in air. Agitation of the pickling bath is necessary in order to achieve a uniform pickling result. A similar process, which differs from the above-described process basically only in the adjusted redox potential, is described in EP-A-582 121.

The aforementioned pickling processes operate technically satisfactorily and have the ecological advantage that they do not emit nitrogen oxides into the atmosphere. An economic disadvantage, however, is the use of hydrogen peroxide as oxidizing agent. On the one hand, the use of hydrogen peroxide increases the costs of the pickling process and, on the other hand, the production of hydrogen peroxide is energy intensive.

It would be desirable to be able to use oxygen or oxygen-containing gases, in the ideal case air, directly for oxidizing the divalent iron in the pickling or passivating baths into the trivalent form. The ecological and economic disadvantages of the known pickling processes would thereby be avoided. Experience in agitating pickling baths by blowing in air shows, however, that, in conventional pickling baths, oxidation of divalent iron does not take place to a sufficient extent. There is therefore a need for improved pickling or

passivating processes in which the oxidation of divalent iron by oxygen is accelerated by suitable bath additives.

EP-A-795 628 describes a process for pickling special steel, in which the divalent iron that is formed is oxidized catalytically to the trivalent state in an external fixed-bed reactor. Pure oxygen or an oxygen-containing gas is used as oxidizing agent. In this process, part of the pickling bath is converted into an oxidation reactor that contains a fixed catalyst. Noble metals, in particular platinum, are used as catalyst. Palladium, ruthenium, rhodium, gold and alloys thereof may in addition be used. The catalytic oxidation of the divalent iron is accordingly effected using a heterogeneous catalyst.

An alternative process has been proposed in WO99/31296, where the catalysis is homogeneous using copper ions as the catalyst. This document teaches a process for the pickling and/or passivation of special steel, the special steel being contacted with an aqueous treatment solution having a pH of less than or equal to 2.5 at a temperature in the range from 30 to 70 °C and which contains 15 to 100 g/l of iron ions, which process is characterized in that the Fe(II) formed during the pickling process is oxidized into the trivalent state by contacting the treatment solution with oxygen in the presence of 50 to 2000 mg/l of copper(II) ions, especially in the presence of about 50 to about 300 mg/l of Cu ions when martensitic or ferritic stainless steel is being pickled.

The latter document also discloses: „The procedure thus makes it possible to use inexpensive oxygen as oxidizing agent in the pickling process and to avoid to a large extent the use of other oxidizing agents, for example hydrogen peroxide. Should a particularly high redox potential of the solution be desirable for particular reasons, it is obviously possible to establish this by adding additional oxidizing agents, for example hydrogen peroxide, persulfates or similarly acting compounds. However, it is preferable and economically particularly advantageous to carry out the process according to the present invention using oxygen as the sole oxidizing agent in order to oxidize Fe(II) to Fe(III).“

Thus, this document teaches that oxygen should be used as the sole oxidizing agent under usual circumstances. Only if „a particularly high redox potential of the solution should be desirable for particular reasons“, the addition of a more strongly oxidizing agent is recommended. This teaching could be interpreted as „only if the redox potential has to

be increased from the pre-established level to a „particular high“ level, this has to be achieved by the addition of additional oxidizing agents.”

Practical experience has shown, however, that when „using oxygen as the sole oxidizing agent in order to oxidize Fe(II) to Fe(III)“, according to the teaching of WO99/31296, the ratio of the concentrations of Fe(III) to Fe(II) and/or redox potential tends to fall slowly during the pickling process. This makes it necessary to add additional strong oxidizing agents at some time, increasing the costs of the pickling process. It would be desirable to have a clear teaching how much additional strong oxidizing agent should be added at which time in order to run the pickling process with the lowest possible costs at technically reasonable efficiency. And it would also be desirable to have this process automated in a way that the addition of the additional strong oxidizing agent is triggered automatically without involving manual action if some pre-established conditions are reached.

These objectives are met by a process for pickling and/or passivating stainless steel in one or more steps, wherein in each step the stainless steel is brought into contact with an aqueous treatment solution with a pH value of 2.5 or below, which contains Fe(III) ions which are reduced to Fe(II) ions during pickling, wherein Fe(II) ions are re-oxidized continuously or discontinuously by the injection of oxygen gas or of a gas mixture containing more than 10 % by volume of oxygen gas into at least a part of the treatment solution, a catalyst being used when the concentration of oxygen gas in the gas mixture is less than 30 % by volume, characterized in that

- a) for each step an optimum Fe(III) concentration or an optimum Fe(III)/Fe(II) weight ratio is determined experimentally or is preset based on experience
- b) the actual Fe(III) concentration or the actual Fe(III)/Fe(II) weight ratio is monitored continuously or discontinuously by analysis or by measuring the redox potential of the aqueous treatment solution,
- c) a non-gaseous oxidizing agent is additionally added to said aqueous treatment solution as long as either the actual Fe(III) concentration is by more than 3 g/l lower than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is by more than 0.15 lower than the optimum Fe(III)/Fe(II) weight ratio, and the addition of the non-gaseous oxidizing agent is terminated when either the actual Fe(III) concentration is equal to or higher than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is equal to or higher than the optimum Fe(III)/Fe(II) weight ratio.

This teaching defines the conditions when, besides oxygen or an oxygen containing gas, an additional non-gaseous strong oxidizing agent should be fed, and how long and/or in which amounts it should be fed. In this way it is guaranteed that the efficiency of the pickling process is maintained, even if completely under automatic control, and at the same time the amount of (relatively expensive) non gaseous oxidizing agent is kept as low as technically possible.

Using a catalyst as described in the above cited state of the art is necessary when the oxygen content of in the gas mixture is less than about 30 % by volume, as it is the case for air. Therefore, if a catalyst is available, for cost reasons air is the preferred oxygen containing gas mixture. If a catalyst is not available or if its use has technical disadvantages, a gas mixture has to be used which contains at least 30 %, preferably at least 50 %, and especially at least 80 % by volume of oxygen. Technical grade oxygen gas is preferably used in this case.

In step a) the „optimum“ Fe(III) concentration or the „optimum“ Fe(III)/Fe(II) weight ratio depend on various other parameters, e.g. the material to be pickled, on the number of pickling steps, the pickling temperature, and the concentrations of the various acids in the pickling bath. Different „optimum“ values are used if there is simultaneous pickling and passivation in one bath or if different pickling and passivation baths are used. As these „optimum“ values are the same for the present invention as for known pickling processes according to the state of the art, they are already known to the expert or can be found out by trials. Thus, the „optimum“ Fe(III) concentration or the „optimum“ Fe(III)/Fe(II) weight ratio can be defined as being those values which give the desired pickling result (e.g. in terms of pickling speed and surface appearance), or if there is a whole range of values which lead to the same pickling result, as the mid-point values within this range. Usually, the optimum Fe(III) concentration will be higher than 5 g/l, preferable higher than 10 g/l, and especially higher than 15 g/l. And it may be lower than 100 g/l, preferably lower than 80 g/l, and especially lower than 70 g/l. Generally, the optimum Fe(III) concentration will increase with an increasing Fe(II) concentration in the bath. Therefore, in a preferred embodiment, the Fe(III) ions are present in a concentration range between 15 and 100 g/l. The optimum Fe(III)/Fe(II) weight ratio will usually be higher than 0.3 when only pickling is desired, and higher than 1.0 if simultaneous pickling and passivation is desired. An upper limit of 10 and especially of 20 will usually not be surpassed in a worked-in pickling solution after the starting phase, in which the ratio may be infinite due to the absence or the very low concentration of Fe(II).

Analytical methods to determine the Fe(III) and Fe(II) concentrations in the pickling solution are known in the art, e.g. manganometric or iodometric redox-titration methods. The Fe(III)/Fe(II) weight ratio is strongly linked to the redox potential of the solution, if other parameters like temperature, free acid and free fluoride ion values are kept constant. Therefore, it is recommended to measure Fe(III)/Fe(II) weight ratio indirectly via the redox potential instead of via direct chemical analysis. A calibration curve can be established which relates the Fe(III)/Fe(II) weight ratio to the redox potential, when the other influencing parameters are kept constant. Any reference electrode (e.g. Ag/AgCl or Kalomel electrodes) may be used, as long as the same electrodes are used for the calibration and the actual measurements.

For example, the process according to the present invention may be operated so that, instead of the ratio of Fe(III) to Fe(II), the redox potential of the solution is used to evaluate whether the solution has a sufficient pickling and/or passivating capability. In order to act in a pickling manner, the treatment solution should have a redox potential of at least 200 mV with respect to a silver/silver chloride electrode. The redox potential is preferably at least 220 mV and in particular at least 250 mV. The upper limit of the potential range to be set may be chosen to be about 800 mV. Treatment solutions having redox potentials below about 350 mV are, in particular, pickling, while treatment solutions having redox potentials of 350 mV and above generally have a passivating action.

The non-gaseous oxidizing agent added in step c) is preferably selected from hydrogen peroxide or compounds which liberate hydrogen peroxide in an aqueous acidic solution, chlorine-oxygen acids with an oxidation state of chlorine of +1 or above, or permanganate salts. As it is common practice in the state of the art, an aqueous solution of hydrogen peroxide will usually be used. Commercial products with hydrogen peroxide concentrations in a range between 30 and 70 weight % may be used. Preferably, the hydrogen peroxide solution is stabilized against the decomposition in metal ion containing acid solutions, or a stabilizer is added separately to the pickling solution. The same stabilizers may be used which are being used according to the state of the art, e.g. phenacetine (i.e. acetyl-p-phenetidine), 8-hydroxyquinoline, sodium stannate, phosphoric acids, salicylic acid, pyridinecarboxylic acids, or the stabilizers described in WO01/49899.

Preferably, to make the process according to the present invention economically as favorable as possible, the injection of the oxygen gas or the gas mixture containing more

than 10 % by volume of oxygen gas is terminated when the actual Fe(III) concentration is by more than 3 g/l higher than the optimum Fe(II) concentration, or when the actual Fe(III)/Fe(II) weight ratio is by more than 0.15 higher than the optimum Fe(III)/Fe(II) weight ratio. This results in additional savings of process costs.

The procedure according to this invention may be applied for pickling solutions with compositions according to the state of the art, containing different amounts of various acids. E.g. the pickling solution may comprise one or more of the following acids as free acids:

20 to 180 g/l of sulfuric acid

1 to 60 g/l of hydrofluoric acid,

0.1 to 120 g/l of hydrochloric acid,

under the proviso that the total free acid concentration is at least 0.5 equivalents/l. "Free acid" means the amount of acid that is not yet used for salt formation with metal cations, i.e. the amount of acid which is still available in the bath for forming salts with freshly dissolved metal ions. A pickling solution comprising sulfuric acid together with hydrofluoric acid is especially preferred. Hydrochloric acid may be additionally present in catalytic amounts, i.e. in amounts from 0.1 to 10 g/l. As outlined in the introduction it is preferred that the pickling solution contains as little nitric acid or nitrate salts as possible, especially no nitric acid at all.

As known in the art (e.g. EP 0776993) it is especially efficient to feed the non-gaseous oxidizing agent into a circuit through which the treatment solution is circulated by action of a pump. Such a circuit is usually present in pickling installations in order to run the pickling solution over a heat exchanger.

In cases where a catalyst is being used, one of the two alternatives cited in the introduction may be used in order to bring the oxygen containing gas in contact with the catalyst and the pickling solution. One alternative is characterized in that at least a part of the treatment solution is fed continuously or discontinuously into a reactor which contains a catalyst in solid form, the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas is injected into this reactor, and the treatment solution is reused for the pickling or passivating after having been in contact with the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas in this reactor. The catalyst may be present in a static or in an agitated bed. Noble metals, in particular platinum, are used as catalyst. Palladium, ruthenium, rhodium, gold and alloys thereof may in addition

be used, as disclosed in EP-A-795 628. Alternatively, if homogeneous catalysis is being applied, a catalyst is added in dissolved form to at least a part of the treatment solution, and this part of the treatment solution is brought into contact with the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas. In this case, the catalyst preferably consists of copper(II) ions which may be added in salt form, e.g. as the sulfate salt. Further details of operation and of Cu ion concentrations are disclosed in the above cited WO99/31296. As stated there, the Cu(II) ion concentration may be in the range of 50 to 2000 mg/l, preferably in the range of 200 to 600 mg/l for austenitic stainless steel. For the pickling of ferritic or martensitic stainless steels, a Cu(II) ion concentration of 50 to 300 mg/l is preferred.

In order to obtain a good mixing efficiency, it is preferred that a part of the treatment solution is circulated through a conduit, and the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas is injected into the conduit by using an injector, e.g. a Venturi system. This feature is especially advisable if oxygen gas or a gas mixture containing more than 30 % by volume of oxygen gas is used, without using a catalyst.

In a special embodiment, the pickling and/or passivating of stainless steel is carried out in two or more steps, and the optimum Fe(III) concentration or the optimum Fe(III)/Fe(II) weight ratio in the aqueous treatment solution is set at a higher value in a subsequent step than in the previous step. This results in a very economic use of the pickling chemicals.

The process of the present invention minimizes the overall costs for the oxidation of Fe(II) ions to Fe(III) ions in order to maintain the pickling activity. It is, therefore, more economic than comparable pickling processes not using the characteristic feature of the present invention for minimizing the amounts of added oxidizing agents.

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Claims

1. A process for pickling and/or passivating stainless steel in one or more steps, wherein in each step the stainless steel is brought into contact with an aqueous treatment solution with a pH value of 2.5 or below, which contains Fe(III) ions which are reduced to Fe(II) ions during pickling, wherein Fe(II) ions are re-oxidized continuously or discontinuously by the injection of oxygen gas or of a gas mixture containing more than 10 % by volume of oxygen gas into at least a part of the treatment solution, a catalyst being used when the concentration of oxygen gas in the gas mixture is less than 30 % by volume, characterized in that
 - a) for each step an optimum Fe(III) concentration or an optimum Fe(III)/Fe(II) weight ratio is determined experimentally or is preset based on experience,
 - b) the actual Fe(III) concentration or the actual Fe(III)/Fe(II) weight ratio is monitored continuously or discontinuously by analysis or by measuring the redox potential of the aqueous treatment solution,
 - c) a non-gaseous oxidizing agent is additionally added to said aqueous treatment solution as long as either the actual Fe(III) concentration is by more than 3 g/l lower than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is by more than 0.15 lower than the optimum Fe(III)/Fe(II) weight ratio, and the addition of the non-gaseous oxidizing agent is terminated when either the actual Fe(III) concentration is equal to or higher than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is equal to or higher than the optimum Fe(III)/Fe(II) weight ratio.
2. A process according to claim 1, characterized in that the non-gaseous oxidizing agent is selected from hydrogen peroxide or compounds which liberate hydrogen peroxide in an aqueous acidic solution, chlorine-oxygen acids with an oxidation state of chlorine of +1 or above, or permanganate salts.
3. A process according to one or both of claims 1 and 2, characterized in that the injection of the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas is terminated when the actual Fe(III) concentration is by more than 3 g/l higher than the optimum Fe(III) concentration, or when the actual Fe(III)/Fe(II) weight ratio is by more than 0.15 higher than the optimum Fe(III)/Fe(II) weight ratio

4. A process according to one or more of claims 1 to 3, characterized in that the Fe(III) ions are present in a concentration range between 15 and 100 g/l.
5. A process according to one or more of claims 1 to 4, characterized in that the aqueous treatment solution contains one or more of the following acids as free acids:
20 to 180 g/l of sulfuric acid
1 to 60 g/l of hydrofluoric acid,
0.1 to 120 g/l of hydrochloric acid,
under the proviso that the total free acid concentration is at least 0.5 equivalents/l.
6. A process according to one or more of claims 1 to 5, characterized in that the non-gaseous oxidizing agent is fed into a circuit through which the treatment solution is circulated by action of a pump.
7. A process according to one or more of claims 1 to 6, characterized in that at least a part of the treatment solution is fed continuously or discontinuously into a reactor which contains a catalyst in solid form, the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas is injected into this reactor, and the treatment solution is reused for the pickling or passivating after having been in contact with the oxygen gas or the gas mixture containing more than 30 % by volume of oxygen gas in this reactor.
8. A process according to one or more of claims 1 to 6, characterized in that a catalyst is added in dissolved form to at least a part of the treatment solution, and this part of the treatment solution is brought into contact with the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas.
9. A process according to one or more of claims 1 to 8, characterized in that a part of the treatment solution is circulated through a conduit, and the oxygen gas or the gas mixture containing more than 10 % by volume of oxygen gas is injected into the conduit by using an injector.
10. A process according to claim 9, characterized that oxygen gas or a gas mixture containing more than 30 % by volume of oxygen gas is used, without using a catalyst.

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11. A process according to one or more of claims 1 to 10, characterized in that the pickling and/or passivating of stainless steel is carried out in two or more steps, and the optimum Fe(III) concentration or the optimum Fe(III)/Fe(II) weight ratio in the aqueous treatment solution is set at a higher value in a subsequent step than in the previous step.

INTERNATIONAL SEARCH REPORT

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PCT/EP 02/09730

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C23G1/36 C23G1/08 C23C22/77 C23C22/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23G C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 31296 A (COMMINELLIS CHRISTOS ;HENKEL KGAA (DE); GIORDANI PAOLO (IT); TRASA) 24 June 1999 (1999-06-24) cited in the application page 8, line 5 -page 13, line 5; claims; examples	1-11
A	IT 1 243 406 B (DEGARA VITTORIO) 10 June 1994 (1994-06-10) page 4, line 5 -page 5, line 7; claims	1-11
A	WO 00 33061 A (HENKEL KGAA ;ACCIAI SPECIALI TERNI SPA (IT); DEMERTZIS IOANNIS (IT) 8 June 2000 (2000-06-08) page 12, line 1 -page 15, line 19; claims	1-11
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Mauger, J

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/09730

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